Iron Complexes with Polythioether Ligands: the Relation of Unusually Large Mössbauer Quadrupole Splittings to Structure†

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New thioether complexes of iron(II) have been prepared: $[Fe(MeCN)_2([14]aneS_4)][FeI_4]$ ($[14]aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane), $[Fe([16]aneS_4)]X_2$ ($[16]aneS_4$ = 1,5,9,13-tetrathiacyclohexadecane) and $[Fe(MeSCH_2CH_2SMe)_2X_2]$ (X = Br or I). The crystal structure of $[Fe([16]aneS_4)]I_2$ and Mössbauer properties of $[Fe([16]aneS_4)]X_2$ are consistent with their formulation as unusual square-planar, high-spin iron(II) complexes. This peculiarity is ascribed to the size of $[16]aneS_4$ which forces longer than normal Fe–S bonds on the system.

The possibility that iron rather than molybdenum might be at the active centre of nitrogenase has stimulated us to attempt to reproduce the dinitrogen chemistry exhibited by molybdenum, but on iron.[1] We have previously explored the chemistry of iron(II) halides with diphosphines to establish a suitable basis for this research.[2] However, we are all too frequently made aware that metal ions in biological systems are never ligated by tertiary phosphines, and that sulfur (generally as sulfide) is likely to be the predominant ligand species. There is an extensive (mainly cluster) chemistry of iron ligated by sulfide and/or thiolate,[3] which we did not wish to enter. We report here on iron(II) complexes with thioethers, which were intended to be a first step towards preparing iron(0) thioether dinitrogen complexes.

Results and Discussion

Initially we attempted to synthesise iron(0) dinitrogen complexes with thioether ligands by direct reaction of the thioethers with $[Fe(C_8H_{12}\text{-}1,5)_2]$ (obtained by metal-vapour synthesis) under N_2.[4] This method has been used to prepare $[Fe(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$,[5] but we could obtain no evidence of stable compounds by this route using either $Ph_2PCH_2CH_2PPh_2$ or 1,4,7,10-tetrathiacyclododecane ($[12]aneS_4$). Consequently, we adopted the strategy of attempting to reduce complexes $[FeX_2S'_4]$, where X = Cl, Br or I, and S′ = a thioether group.

Compounds were obtained by direct reaction of the anhydrous iron halide with a dithioether or tetrathioether in an appropriate solvent. Thus, reaction of FeX_2 (X = Br or I) with 2,5-dithiahexane in ether yielded paramagnetic $[FeX_2(MeSCH_2CH_2SMe)_2]$. These complexes presumably have a *trans* stereochemistry, like their diphosphine analogues. Neither reduction of $[FeX_2(MeSCH_2CH_2SMe)_2]$ by $NaBH_4$ in EtOH, nor reaction with $NaBPh_4$ in MeOH, both under N_2, appeared to yield a dinitrogen complex. Due to the powerful stench of the dithioethers we transferred our attention to the derivatives of the non-volatile crystalline tetrathioethers 1,5,9,13-tetrathiacyclohexadecane ($[16]aneS_4$) and 1,4,8,11-tetrathiacyclotetradecane ($[14]aneS_4$). The adducts with FeX_2 which we prepared were found, upon attempted reduction to give dinitrogen complexes, to decompose.

However, the preparations of the adducts themselves yielded results which were very unexpected. For example, the reaction of FeX_2 and $[14]aneS_4$ in MeCN was only successful for X = I. For X = Cl or Br we observed no reaction. The only complex we obtained analysed for $[Fe(MeCN)_2([14]aneS_4)][FeI_4]$, which shows no band assignable to ν(CN) in the IR spectrum, but presumably has a *trans* cation stereochemistry. The reaction is reminiscent of that of $Ph_2PCH_2CH_2PPh_2$ (dppe) with FeI_2 in MeCN, which yields $[Fe(MeCN)_2(dppe)_2][FeI_4]$,[6] and our product can be formulated and behaves as expected. The Mössbauer spectrum (77 K), Fig. 1, is consistent with this formulation, revealing an unresolved doublet with a centre shift of 0.46 mm s^{-1} and a doublet centred at 0.92 mm s^{-1} with a quadrupole splitting of 2.62 mm s^{-1}. Centre shifts of 0–0.5 mm s^{-1} are consistent with low-spin octahedral iron(II), which occasionally exhibits small, unresolved quadrupole splittings. The resolved quadrupole doublet is assignable to high-spin tetrahedral iron(II),[7] and thus the compound appears unexceptional. The molar conductivity in nitromethane is rather low for a 1:1 electrolyte, but, of course, very large ions are involved.

In contrast the adducts $FeX_2\cdot[16]aneS_4$ (X = Br or I]) were obtained from FeX_2 and $[16]aneS_4$ in boiling MeCN. The homologue with X = Cl was not obtained, since $FeCl_2$ did not react with $[16]aneS_4$ in MeCN. Although both adducts were prepared in boiling MeCN, there was no MeCN co-ordinated, a very unexpected observation. The compounds are paramagnetic at room temperature, μ_{eff} = 5.8(Br) and 5.1(I) respectively, consistent with about four unpaired electrons, based on the spin-only formula. This suggests high-spin iron(II) rather than the expected low spin.

The Mössbauer spectra at 77 K, Fig. 2, consist of quadrupole doublets with centre shifts 0.96(Br) and 0.94(I) and quadrupole splittings 3.60(Br) and 4.10(I) mm s^{-1}. At 295 K the spectra are similar. Such large splittings have, in the past, been claimed as characteristic of five-co-ordinate high-spin iron(II).[8] However, the molar conductivity of $FeI_2\cdot[16]aneS_4$ in nitromethane (165 ohm^{-1} cm^2 mol^{-1}) is in the range normally ascribed to 1:2 electrolytes.[9] We therefore decided to undertake an X-ray crystal structure analysis, the results of which have been re-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

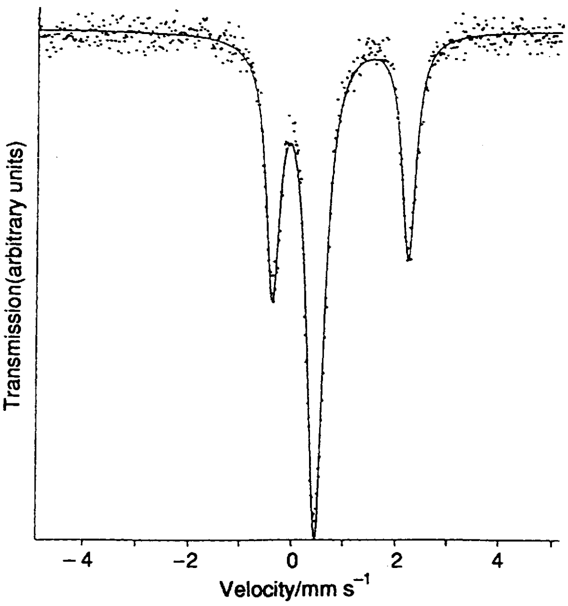

Fig. 1 Mössbauer spectrum of $[Fe(MeCN)_2([14]aneS_4)][FeI_4]$ at 77 K, showing the doublet due to the tetrahedral high-spin $[FeI_4]^{2-}$ anion and the unresolved doublet for $[Fe(MeCN)_2([14]aneS_4)]^{2+}$

Table 1 Final atom coordinates (fractional $\times 10^4$) for $[Fe([16]aneS_4)]I_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Fe	0	0	0
I	1878.2(2)	405.7(1)	2651.0(2)
S(1)	−446.4(8)	−1689.7(4)	893.4(6)
C(11)	−2871(3)	−1835(2)	831(3)
C(12)	−3760(3)	−1355(2)	2103(3)
C(13)	−3118(4)	−334(2)	2542(3)
S(2)	−2922.8(8)	473.7(4)	1006.7(7)
C(21)	−2631(4)	1650(2)	1899(3)
C(22)	−2156(3)	2471(2)	875(3)
C(23)	−174(3)	2535(2)	500(3)

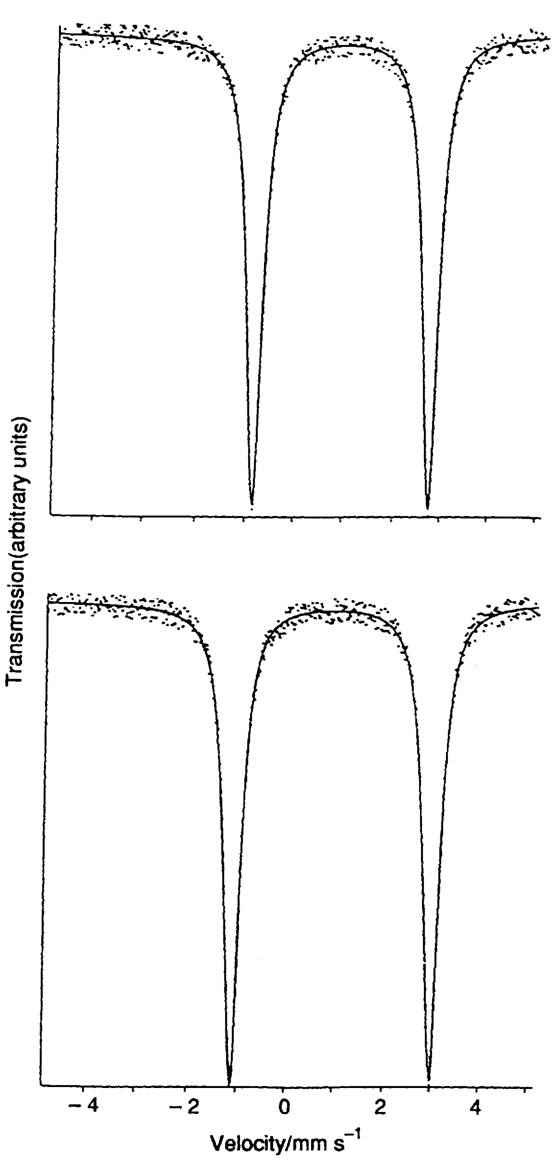

Fig. 2 Mössbauer spectra of $[Fe([16]aneS_4)]Br_2$ (above) and $[Fe([16]aneS_4)]I_2$ (below) at 77 K

ported in preliminary form.[10] The structure is shown in Fig. 3, and atomic coordinates and bond dimensions are in Tables 1 and 2, respectively.

Let us first consider the iron–iodine separations. The octahedral ionic radius of Fe^{II} is 0.78 Å for high spin, and the radius for I is 2.16 Å.[11] The sum is close to the observed Fe–I separation (2.89 Å) reported here. Values for the covalent Fe–I separation of 2.706(1) and 2.641(7) Å are in the literature.[2] In FeI_2 the reported separation is 2.88 Å.[12] We therefore regard the bonding in this compound as close to that in FeI_2. Our complexes are so reluctant to become six-co-ordinate that they crystallise from acetonitrile without co-ordinated MeCN, and they are 1:2 electrolytes in nitromethane. This means that this compound constitutes a rare example of square-planar iron(II). The complexes $[FeCl_2(PHEt_2)_2]$,[13] $[FeCl_2\{PH_2(C_6H_{11})\}_2]$[14] and $[Fe\{PH_2(C_6H_{11})\}_4]^{2+}$ (ref. 15) have been suggested to be square planar on the basis of magnetic data. They have μ_{eff} *ca.* 3, which is consistent with an intermediate ($S = 1$) spin state, rather than moments μ_{eff} of *ca.* 5, as with our compounds.

The evidence of structure and physical properties suggest that our complex is closer to an ionic high-spin square-planar form than to an octahedral. As far as we can judge, the only other unequivocal example of square-planar high-spin iron(II) is in the mineral gillespite $BaFeSi_4O_{10}$, in which iron is co-ordinated by four oxygen atoms, with the nearest axial atoms to any given Fe^{II} being other Fe^{II} atoms at a distance of over 8 Å.[16] The magnetic moment per iron atom in gillespite is 5.12, very similar to our values, and this emphasises that these spin-only values for iron(II) do not necessarily imply tetrahedral or five-co-ordination.[17]

It remains to discuss why $[16]aneS_4$ should produce these unexpected structural and chemical effects when $[14]aneS_4$ yields the expected low-spin, octahedral adducts and strong axial co-ordination. Consideration of the angles and bond lengths within the co-ordinated thioether shows some evidence of strain. The thioether has almost perfect $2/m$ symmetry with the pseudo-two-fold axis passing through the iron and the C(12) and C(12′) atoms. The angles within the ring at the methylene carbon atoms are slightly greater than tetrahedral, as might have been expected. The carbon–carbon bond lengths are normal single-bond lengths, as are those of the carbon–sulfur bonds. The conformation of the thioether is novel, but there are no bond compressions or extensions. However, there is evidence of strain from the dihedral angles between the planes subtended by the adjacent bonds at the S–C and C–C bonds. Those at the S–C bonds are close to 180°, as would be expected, but those at the C–C bonds show a wide range of values. For example, at C(11)–C(12) and C(12)–C(13) the absolute value of the dihedral angle is *ca.* 45°, rather than the 60° of an ideal *gauche* conformation, whereas about C(21)–C(22) and C(22)–C(23) it is *ca.* 82°. Here there is some deformation strain.

The origin of the peculiar properties of our system is not likely

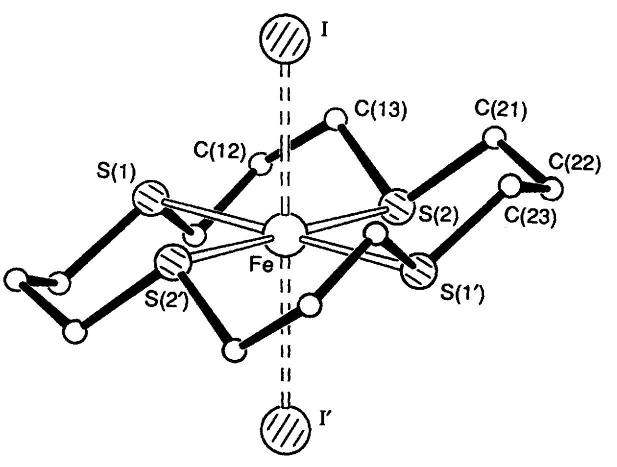

Fig. 3 The molecular arrangement of atoms in Fe([16]aneS_4)]I_2, showing atom numbering. There is doubt over the nature of the Fe–I bonds

Table 2 Bond dimensions (lengths in Å, angles in °) in [Fe([16]aneS_4)]I_2 with e.s.d.s in parentheses

(*a*) Co-ordination sphere of the iron

Fe–I	2.8896(2)	I–Fe–S(1)	87.3(1)
Fe–S(1)	2.475(1)	I–Fe–S(2)	92.2(1)
Fe–S(2)	2.485(1)	S(1)–Fe–S(2)	89.2(1)

(*b*) 1,5,9,13-Tetrathiacyclohexadecane ligand

S(1)–C(11)	1.825(3)	S(2)–C(21)	1.819(3)
C(11)–C(12)	1.527(4)	C(21)–C(22)	1.523(4)
C(12)–C(13)	1.526(4)	C(22)–C(23)	1.534(3)
C(13)–S(2)	1.823(3)	C(23)–S(1')	1.811(3)
Fe–S(1)–C(11)	103.3(1)	Fe–S(2)–C(13)	103.3(1)
Fe–S(1)–C(23')	107.9(1)	Fe–S(2)–C(21)	107.8(1)
C(23')–S(1)–C(11)	100.2(1)	C(13)–S(2)–C(21)	100.2(1)
S(1)–C(11)–C(12)	112.1(2)	S(2)–C(21)–C(22)	112.6(2)
C(11)–C(12)–C(13)	117.6(2)	C(21)–C(22)–C(23)	115.2(2)
C(12)–C(13)–S(2)	111.4(2)	C(22)–C(23)–S(1')	113.1(2)

(*c*) Torsion angles in the thioether ring

C(23')–S(1)–C(11)–C(12)	168.6(2)
S(1)–C(11)–C(12)–C(13)	44.2(3)
C(11)–C(12)–C(13)–S(2)	46.0(3)
C(12)–C(13)–S(2)–C(21)	168.3(2)
C(13)–S(2)–C(21)–C(22)	171.7(2)
S(2)–C(21)–C(22)–C(23)	−82.4(3)
C(21)–C(22)–C(23)–S(1')	82.3(3)
C(22)–C(23)–S(1')–C(11')	−171.3(2)

Primed atoms are of the opposite half of the macrocycle, with coordinates −*x*, −*y*, −*z*.

to be the iodine atoms. The shortest contacts between iodine and the thioether methylene hydrogen atoms are *ca.* 0.3 Å shorter than the sum of the van der Waals radii,[18] and the approaches to neighbouring thioethers are a little longer. However, the Fe–S separations are about 0.1–0.2 Å longer than in other iron–sulfur (thioether) compounds, though these are not for high-spin compounds.[19] We interpret all this as showing that the iron atom is distorting the cyclic thioether, by drawing in all four sulfur atoms, but that the intensity of this interaction is not sufficient to enable 'normal' iron–sulfur bonds to be formed. They are longer than usual, and the ligand field exerted by the thioether must be rather weak. Some confirmation of weak bonding is the fact that when we tried to reduce [Fe([16]aneS_4)]I_2 to iron(0) in an attempt to prepare iron(0) dinitrogen complexes, reducing agents such as sodium amalgam, sodium dihydronaphthylide, and sodium tetrahydroborate caused degradation of the thioether and the production of metallic iron.

Somewhat similar observations have been made in other areas of macrocyclic chemistry. Thus [16]aneN_4 (1,5,9,13-tetraazacyclohexadecane) reacts with iron(II) in acetonitrile to yield high-spin [Fe(MeCN)$_2$([16]aneN_4)]$^{2+}$, whereas [14]ane-N_4 (1,4,8,11-tetraazacyclotetradecane) produces [Fe(MeCN)$_2$-([14]aneN_4)]$^{2+}$, which is low spin. Presumably the smaller macrocycle exerts the stronger ligand field.[20]

The usual ligand-field splittings for a square-planar complex are generally taken to be $d_{z^2} < d_{xy},d_{yz} < d_{xy} < d_{x^2-y^2}$. This could give the appropriate spin-only value of μ_{eff} in our complex. If, on the other hand, the complex is regarded as octahedral, and the sulfur atoms as exhibiting a displacement along the Fe–S vectors away from the 'ideal' positions while maintaining a centre of symmetry, then a different ordering of orbitals, *viz.* $d_{xy} < d_{xz},d_{yz} < d_{x^2-y^2} < d_{z^2}$ might be expected. This could equally well explain the magnetic moment of 5.1, but double occupancy of d_{z^2} is at least consistent with the long Fe–I separations and the non-co-ordination of MeCN. If the odd electron is in d_{xy}, then the usual theory[21] suggests that the sign of the electric field gradient (e.f.g.) should be positive, whereas if it is d_{z^2} it should be negative.

Only a determination of the sign of the e.f.g. will distinguish between these situations. The mineral gillespite, the system most likely to be comparable to ours, contains well defined high-spin, square-planar iron(II). The magnetic moment is 5.12 ± 0.05, with four iron–oxygen separations of 1.97 Å in the square plane, and the next closest approaches being 3.98–4.75 Å. This is imposed by the layer structure of the silicate.[16] In oxides and silicates the normal Fe–O distance is *ca.* 2.14 Å, and the summed covalent radii of iron and oxygen would appear to be at least 2.0 Å. The ground state has been shown to be $^5A_{1g}$ with d_{z^2} lowest, as expected for a square-planar compound, although a ^5E_g excited state has also been detected in the UV spectrum, about 1000 cm^{-1} above the ground state.[17]

If gillespite is a compressed square plane rather than a stretched square plane, as in our case, this might well be expected to increase the energies of $d_{x^2-y^2}$ and d_{xy} and d_{zy} disproportionately compared to the spherically symmetrical case, but since they are, in any case, the d orbitals of highest energy the order should not change, and we might still expect a large quadrupole splitting. In fact, a value of 0.65 mm s^{-1} has been reported, which is very small for a high-spin iron(II) system, and has been ascribed to valence and lattice contributions to the quadrupole splitting of opposite sign and of comparable magnitude.[17] This would be unusual, since the lattice contribution is normally expected to be about 10% of the valence contribution, and this appears to hold in other iron(II) complexes we have studied.[22] Apparently, our case represents a situation where the lattice contribution is 'normal' in magnitude.

In the cases where quadrupole splittings as large as ours have been reported,[8,23–26] these are for high-spin five-co-ordinate iron(II), and the measured e.f.g. is positive. Our work shows that large quadrupole splittings of the order of 4 mm s^{-1} cannot be used to distinguish between high-spin, square-planar and square-pyramidal co-ordination, contrary to the claim[8] that such splittings are characteristic of the latter. The small temperature-dependence of the quadrupole splitting for both iodide and bromide suggests that the ground state is well separated from any excited states. We suggest that such large quadrupole splittings may arise whenever the sixth electron is in a d_{xy} or d_{z^2} orbital and the ground state is well separated from any excited states.

Experimental

All operations were carried out under dry dinitrogen following standard Schlenk techniques. All the solvents were distilled under N_2 from the appropriate drying agents prior to use.

Infrared spectra were recorded in Nujol mulls or in solution on a Perkin-Elmer 882 instrument. Analyses were by Mr. C. J. Macdonald of the Nitrogen Fixation Laboratory, using a Perkin-Elmer 2400 CHN elemental analyser. Mössbauer spectra were recorded on an E.S. Technology MS-105 spectrometer with a 25 mCi ^{57}Co source in a rhodium matrix, at 77 K and referenced against iron foil at 298 K. Magnetic moment determinations were in solution by the Evans method[27] and in the solid state using a Faraday balance.

1,4,8,11-Tetrathiacyclotetradecane, 1,4,7,10-tetrathiacyclododecane and 1,5,9,13-tetrathiacyclohexadecane were purchased from Aldrich Chemicals and used without further purification.

1,5,9,13-*Tetrathiacyclohexadecaneiron*(II) *Diiodide*.—To FeI_2 (0.97 g, 3 mmol) in acetonitrile, solid [16]aneS_4 (1 g, *ca.* 3 mmol) was added. The solution was stirred at room temperature, and a yellow precipitate gradually formed. The reaction mixture was stirred overnight at room temperature. The yellow product was filtered off, washed with diethyl ether and hexane and dried *in vacuo*. Continuous extraction of the crude product with boiling acetonitrile and cooling to −20 °C afforded yellow crystals of the product. Yield: 1.45 g (80%) (Found: C, 23.4; H, 3.9. $C_{12}H_{24}FeI_2S_4$ requires C, 23.7; H, 3.9%). IR (CsI disk): 2912, 2838, 1447, 1428, 1312, 1293, 1256, 1200, 1148, 1073, 1048, 1013, 988, 945, 926, 870, 852, 773, 721, 697, 612, 448, 411, 322, 301 and 230 cm^{-1}.

1,5,9,13-*Tetrathiacyclohexadecaneiron*(II) *Dibromide*.—Iron(II) bromide (0.42 g, 1.8 mmol) in acetonitrile was treated with solid [16]aneS_4 (0.58 g, 1.9 mmol). The reaction was initiated by heating to boiling point, then it was allowed to proceed at room temperature for 12 h. A white solid was obtained, which was filtered off, washed with ether and hexane and dried *in vacuo*. Recrystallisation from acetonitrile afforded pale orange crystals. Yield: 0.67 g (73%) (Found: C, 28.7; H, 4.7. $C_{12}H_{24}Br_2FeS_4$ requires C, 28.2; H, 4.7%). IR (CsI disk): 2910, 2841, 1447, 1429, 1294, 1257, 1150, 1051, 930, 871, 853, 777, 698 and 451 cm^{-1}.

Bis(*acetonitrile*)(1,4,8,11-*tetrathiacyclotetradecane*)*iron*(II) *Tetraiodoferrate*(II).—To a stirred solution of FeI_2 (0.25 g, *ca.* 0.9 mmol), solid [14]aneS_4 (0.12 g, 0.45 mmol) was added. The reaction mixture was heated under reflux for a few minutes in order to start the reaction, then it was stirred overnight at room temperature. Addition of diethyl ether and cooling to −20 °C afforded a magenta crystalline solid which was filtered off, washed with ether and dried *in vacuo*. Yield: 0.21 g (48%) (Found: C, 17.6; H, 2.7; N, 3.3. $C_{12}H_{26}Fe_2I_4N_2S_4$ requires C, 17.3; H, 2.7; N, 2.9%). IR: no $\nu(C{\equiv}N)$ visible in the spectrum, bands at 1437, 1405, 1272, 1018, 909, 862 and 819 cm^{-1}. $\Lambda(MeNO_2) = 36\ \Omega^{-1}\ cm^2\ mol^{-1}$. If this reaction is carried out with an FeI_2 : thioether ratio of 1 : 1, $[Fe(MeCN)_2([14]aneS_4)][FeI_4]$ is obtained together with unreacted thioether.

2,5-*Dithiahexane*, $MeSCH_2CH_2SMe$.—Metallic sodium (11.5 g, 0.5 mmol) was dissolved in absolute ethanol (400 cm^3). To the resulting NaOEt–EtOH solution, ethane-1,2-dithiol (21 cm^3, *ca.* 0.25 mmol) was added dropwise from a dropping funnel and then methyl iodide (31 cm^3, 0.5 mmol), slowly. The mixture was heated under reflux for 2 h. Ethanol was then distilled off at normal pressure and the 2,5-dithiahexane was distilled *in vacuo*, and then purified by trap-to-trap distillation. Yield: 85%. Density $\approx$1.9 g cm^{-3} (8.2 mmol cm^{-3}). IR: 2967, 2914, 2833, 1419, 1321, 1268, 1205, 1133, 1012, 959, 801, 736 and 684 cm^{-1} (liquid film).

CAUTION: All glassware in contact with this compound must be decontaminated by immersion in diluted sodium hypochlorite, in order to remove the horrible smell.

Dibromobis(2,5-*dithiahexane*)*iron*(II).—To a stirred suspension of $FeBr_2$ (2.9 g, 13.5 mmol) in diethyl ether, 2,5-dithiahexane (3.3 cm^3, *ca.* 28 mmol) was added *via* a syringe. The mixture was stirred for 24 h. A white precipitate was obtained, which was filtered off, washed with copious amounts of hexane and dried *in vacuo*. The product was recrystallised from a concentrated tetrahydrofuran solution. Yield: 4.3 g (69%) (Found: C, 20.5; H, 4.4. $C_8H_{20}Br_2FeS_4$ requires C, 20.9; H, 4.4%). IR: 1413, 1264, 1026, 961, 881, 849, 722, 646 and 440 cm^{-1}.

The complex bis(2,5-dithiahexane)diiodoiron(II) was obtained from FeI_2 by a similar procedure in 75% yield (Found: C, 17.2; H, 3.6. $C_8H_{20}FeI_2S_4$ requires C, 17.3; H, 3.6%). IR: 1423, 1404, 1293, 1026, 961, 880, 843 and 645 cm^{-1}.

X-Ray Structure Determination of $[Fe([16]aneS_4)]I_2$.—*Crystal data*. $C_{12}H_{24}FeI_2S_4$, $M = 606.2$; monoclinic, space group $P2_1/c$ (no. 14), $a = 7.4831(6)$, $b = 13.6242(8)$, $c = 9.3983(6)$ Å, $\beta = 91.133(6)°$, $U = 958.0$ Å^3, $Z = 2$, $D_c = 2.101$ g cm^{-3}, $F(000) = 584$, μ(Mo-Kα) = 43.8 cm^{-1}, λ(Mo-Kα) = 0.710 69 Å.

The crystals are small yellow parallelepipeds. One, *ca.* 0.14 × 0.11 × 0.16 mm, was mounted on a glass fibre. After preliminary photographic examination accurate cell dimensions were refined from the goniometer settings of 25 reflections (θ *ca.* 14°) on our Enraf-Nonius CAD4 diffractometer (with monochromated radiation). Diffraction intensities were recorded to $\theta_{max} = 25°$. Corrections were made for Lorentz and polarisation effects. The crystal showed no sign of deterioration during the data collection.

The complete set of 1685 unique data were entered into the SHELX program system[28] where absorption corrections were applied from measurements of the crystal. The structure was solved by the heavy-atom method and all atoms were refined by full-matrix least-squares methods; the non-hydrogen atoms were allowed anisotropic thermal parameters, and hydrogen atoms were refined isotropically and independently. At convergence, $R = R' = 0.019$[28] for all data, weighted $w = \sigma_F^{-2}$. There were no features of significance in the final difference map.

Scattering factors for neutral atoms were taken from ref. 29. Computer programs, noted above and in Table 4 of ref. 30, were run on the MicroVAX II in our Laboratory.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters, and remaining bond lengths and angles.

Acknowledgements

This work was carried out with support from the European Economic Community Science Programme, Grant ST2*410 (to M. J.-T.). We thank Dr. D. J. Evans of the Nitrogen Fixation Laboratory for obtaining the Mössbauer spectra.

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Received 11*th February* 1992; *Paper* 2/00707J